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USE OF AMINO ACID ANALYSIS FOR ESTIMATION OF BERRY JUICE AUTHENTICITY

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Abstract. Free amino acid contents: aspartic acid, threonine, serine, glutamic acid, proline, glycine, alanine, valine, methionine, isoleucine, leucine, tyrosine, γ-aminobutyric acid, histidine, lysine and arginine in juices of three strawberry varieties ('Senga', 'Ducat', 'Marmolada'), raspberry ('Beskid', 'Canby', 'Malling Seedling'), black currant ('Ben Lomond', 'Titania', 'Ojebyn') and red currant ('Rondom', 'Jonker', 'Holenderska') were determined in this paper. Examinations were performed in three following years: 1998, 1999 and 2000, by use of HPLC method. Achieved amino acid contents were compared with standard values contained in Code of Practice. Significantly higher aspartic acid and glutamic acid concentrations of standard values published in Code of Practice were found in examined strawberry and black currant juices. Selected amino acids can be used for estimation of berry juices authenticity. Serine, valine and methionine can be the indicator of addition of strawberry juice to raspberry juice, aspartic acid and serine – addition of red currant juice to raspberry juice and aspartic acid and methionine – addition of strawberry juice to black currant juice. Adulteration of black currant juice with red currant juice cannot be detected on the base of amino acid contents.

Key words: amino acids, HPLC, berry fruits, juices, adulterations

INTRODUCTION

Fruit juice adulterations make serious ethical and economic problem. Consumers suffer from losses, because they expect products of standard value and authentic, as well as honest producers losing at dishonest competition [Fügel et al. 2004, Nagy et al. 1988, Nagy 1997, Neuhäuser 2000, Przybyla 1989, Wrolstad 1991].

Producers, by adulteration of juices, decrease the costs of raw materials and achieve higher economic profit. The average prices paid by industry for fruits in 1992-1999 were: raspberries – 2.17 zl/kg, black currants – 1.33 zl/kg, strawberries – 1.25 zl/kg and red currants – 0.91 zl/kg [Kubiak 2000]. The wholesale prices of fruits in Germany on 28 June 1999 were: raspberries – 9.0-12.0 DM/kg, black currants – 6.0-7.0 DM/kg,

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strawberries – 2.4-3.4 DM/kg and red currants – 3.0-4.8 DM/kg [FAMMU/FAPA... 1999]. The above data indicate that expensive juices can be particularly exposed to adulterations, just like raspberry and black currant juices.

Fruit juices are adulterated by addition of water, sugar, acid, synthetic taste and aromatic substances, dyes, extracts of peels and foots, as well as cheap juices. The basic detection method of adulterations of fruit juices is comparison of their chemical composition with standard values, for example those contained in Code of Practice [1996]. Code of Practice publishes absolute quality requirements (for example density, contents of heavy metals) and tolerance concentrations of different components, for example free amino acids in authentic fruit juices [Czapski and Tyma 1996, Martinek 1998, Neuhäuser 2000, Niewiarowicz 2000, Obiedziński 1998, Płocharski 2000, Stój et al. 2001, Targoński 2000].

Contents of particular amino acids are different for different juices, so they can be the indicators of their authenticity. By comparison of determined amino acid concentrations with standard values published in Code of Practice [1996], it can be found out whether the examined juice is authentic or adulterated. Deviations from accepted norms are the indicators of non-declared juice addition.

Most often analysis of free amino acid contents is performed by means of amino acid analyser, using liquid chromatography [Wallrauch and Faethe 1988]. Selected individual amino acids can be determined by simple chemical [Wallrauch 1976] and enzymatic methods [Boehringer Mannheim... 1986, Henniger 2003]. Adulterations of black currant, red currant, strawberry, raspberry, blackberry, bilberry juices with cheap grape concentrate can be detected on the base of proline analysis. Increasing contents of proline in relatively deficit black currant, red currant and raspberry juices indicate the presence of other fruit juices. Red currants contain higher level of arginine and alanine than black currants, therefore inauthenticity of black currant juices can be easily detected. Characteristic is the lack of difference in contents of proline among bilberries: cultivated and wild growing, though chromatograms of free amino acids distinctly differentiate. Cultivated bilberries contain higher level of arginine, glutamic acid and alanine than wild growing ones [Wallrauch and Faethe 1988].

Free amino acid contents: aspartic acid, threonine, serine, glutamic acid, proline, glycine, alanine, valine, methionine, isoleucine, leucine, tyrosine, γ-aminobutyric acid, histidine, lysine and arginine in authentic strawberry, raspberry, black currant and red currant juices were determined in this paper. Achieved amino acid contents were compared with standard values contained in Code of Practice [1996]. The aim of present paper was to indicate these amino acids, which can be used for estimation of berry juice adulterations. Examinations were performed in three following years: 1998, 1999 and 2000.

MATERIAL AND METHODS

Four berry species were collected in 1998, 1999 and 2000. Strawberries (*Fragaria ananassa*) of 'Senga', 'Ducat' and 'Marmolada' cv. originated from the plantation in Zemborzyce. Raspberries (*Rubus idaeus*) of 'Beskid', 'Canby' and 'Malling Seedling' cv. as well as black currants (*Ribes nigrum*) of 'Ben Lomond', 'Titania' and 'Ojebyn' cv. were from The Experimental Farm in Felin. Red currants (*Ribes rubrum*) of 'Ron-

dom' and 'Holenderska' cv. were collected in garden in a Klementowice and 'Jonker' cv. was collected in Góra Puławska.

Berry fruits were stored in the refrigerator at –28°C. Juices were made from fruits defrosted at ambient temperature in the juice extractor Zelmer 277.8 and then centrifuged in centrifuge MPW 365 for 15 min at 4°C at 11 000 rpm.

Column with ion exchanger Dowex 2 × 8 (Fluka) was prepared. About 30-50 g of Dowexu was suspended in distilled water and by way of decantation small molecules of resin were removed. Ion exchanger was washed with 1M HCl and again it was suspended in double volume of distilled water. Water suspension of ion exchanger was moved to a glass column of size 200 × 20 mm to obtain the layer of 20 mm height. The column was washed with 15 ml of 1 M HCl, and then with distilled water to neutral reaction of eluate. In case when column was not immediately used, ion exchanger was covered with several-millimeter layer of water.

Protein from 2 ml of juice was removed, by addition of 5 ml of 1% picric acid. Mixture was shaken for several seconds and filtered under vacuum. Filtrate was passed through previously prepared column with ion exchanger. Walls of column were washed five times with 3 ml of 0.02M HCl. Eluate from column was collected in round-bottom flask. Flask content was concentrated in a rotary evaporator with water bath at 50°C, to obtain clammy residue. Clammy residue was moved to ampoules, using 12 ml of 6M HCl. The ampoules were sealed and hydrolysis was carried out at 110°C for 20 h. Hydrolyzate was filtered on funnel G-5, poured into round-bottom flask, added 0.5 ml norleucine at concentration of 100 μmol·l^{-1} (internal standard) and evaporated in evaporator at 20°C. Residue was washed with distilled water, again evaporated and dissolved in 5 ml of citrate buffer at pH 2.95.

Analysis of free amino acid contents was performed by means of automatic analyser of amino acids Mikrotechma 339M. For separation of amino acids, column filled with ion exchanger Ostion LG ANB was used. Column was stabilized by alkali lye from 6 to 36 min. After dosage of sample at 36 min, amino acids were washed by citrate buffers of different pH: 36-53 min – buffer of pH 2.95, 53-78 min – buffer of pH 4.25, 78-135 min – buffer of pH 9.45. Flow rate of citrate buffers – 20 ml/h, photometric detection at 570 nm wavelength.

Contents of free amino acids were calculated according to the equation:

$$c = \frac{\frac{P_a}{P_n} \cdot KF \cdot n \cdot r}{v}$$

c – amino acid concentration, mmol·l^{-1},
P_a – amino acid area, mm^2,
P_n – norleucine area, mm^2,
KF – corrective coefficient,
n – norleucine concentration, 50 nmol/0.5 ml,
r – dilution factor,
v – sample volume, ml.

Determination results were statistically worked out using Tuckey's test at significance level $\alpha = 0.05$.

RESULTS AND DISCUSSION

Aspartic acid and glutamic acid were the main amino acids in strawberry juices (Fig. 1). Contents of aspartic acid in strawberry juices in particular years were from 1.68 mmol·l^{-1} to 6.64 mmol·l^{-1} (Table 1) and glutamic acid – from 0.33 mmol·l^{-1} to 2.32 mmol·l^{-1}. Instead, proline, valine (Table 3), methionine (Table 4), isoleucine, leucine, tyrosine, lysine and arginine occurred in small concentrations in strawberry juices.

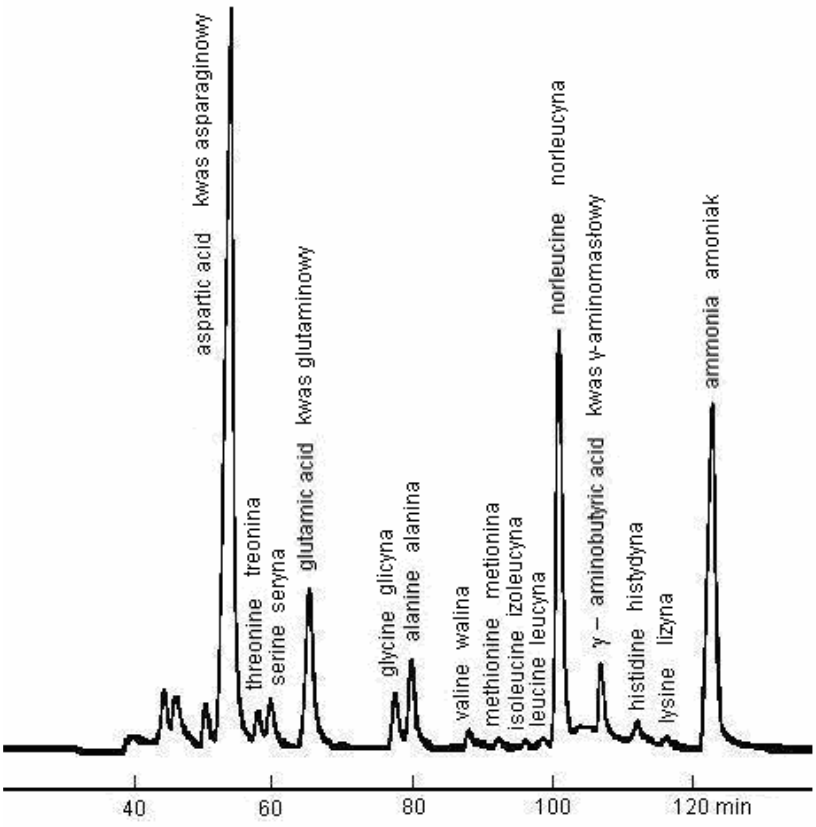

Fig. 1. Chromatogram of amino acids contained in strawberry juice of 'Senga' cv. harvested in 2000
Rys. 1. Chromatogram aminokwasów zawartych w soku truskawkowym odmiany 'Senga' ze zbioru w 2000 roku

The largest concentrations of aspartic acid, serine, glutamic acid and alanine were determined in raspberry juices (Fig. 2). Contents of aspartic acid in raspberry juices in particular years ranged from 1.34 mmol·l^{-1} to 15.61 mmol·l^{-1} (Table 1), serine – from 0.58 mmol·l^{-1} to 1.43 mmol·l^{-1} (Table 2), glutamic acid – from 1.16 mmol·l^{-1} to 2.99 mmol·l^{-1} and alanine – from 0.82 mmol·l^{-1} to 2.92 mmol·l^{-1}. Several amino acids occurred in small concentrations: proline, methionine (Table 4), isoleucine, leucine, tyrosine

Table 1. Contents of aspartic acid in berry juices in 1998, 1999, 2000
Tabela 1. Zawartości kwasu asparaginowego w sokach z owoców jagodowych badanych w latach 1998, 1999, 2000

Type of juice Rodzaje soków	Fruit variety Odmiany owoców	Aspartic acid, mmol·l^{-1} – Kwas asparaginowy, mmol·l^{-1}			
		year of fruit harvest lata zbioru owoców			average średnie
		1998	1999	2000	
Strawberry juice Sok z truskawek	Senga	4.50	6.64	3.37	4.84 ^{AB} ± 1.66
	Ducat	5.06	4.88	6.35	5.43 ^{AB} ± 0.80
	Marmolada	5.02	3.14	1.68	3.28 ^{A} ± 1.67
Raspberry juice Sok z malin	Beskid	2.00	1.99	1.34	1.78 ^{A} ± 0.38
	Canby	3.55	1.57	3.90	3.01 ^{A} ± 1.26
	Malling Seedling	7.82	4.94	15.61	9.46 ^{B} ± 5.52
Black currant juice Sok z czarnych porzeczek	Ben Lomond	0.55	0.18	0.34	0.36 ^{A} ± 0.19
	Titania	0.69	0.21	0.64	0.51 ^{A} ± 0.26
	Ojebyn	1.54	0.39	0.59	0.84 ^{A} ± 0.61
Red currant juice Sok z czerwonych porzeczek	Rondom	0.92	0.41	0.45	0.59 ^{A} ± 0.28
	Jonker	0.26	0.36	0.51	0.38 ^{A} ± 0.13
	Holenderska	0.23	0.26	0.25	0.25 ^{A} ± 0.02

Values in the columns with different letters are significantly different at α = 0.05.
Wartości w kolumnach oznaczone różnymi różnią się literami istotnie przy α = 0,05.

and lysine. Statistical analysis indicated that raspberry juices of 'Beskid', 'Canby' and 'Malling Seedling' cv. significantly differed from average contents of several amino acids. The average aspartic acid and arginine contents for three years of examinations in juices of 'Malling Seedling' cv. (9.46 mmol·l^{-1} and 0.66 mmol·l^{-1}, respectively) were significantly higher in comparison with the average contents of these amino acids in juices of 'Beskid' (1.78 mmol·l^{-1} and 0.22 mmol·l^{-1}, respectively) and 'Canby' cv. (3.01 mmol·l^{-1} and 0.27 mmol·l^{-1}, respectively). Juices of 'Beskid' cv. contained significantly lower average concentrations of threonine, serine, alanine and valine (0.31 mmol·l^{-1}, 0.80 mmol·l^{-1}, 1.56 mmol·l^{-1} and 0.20 mmol·l^{-1}, respectively) in comparison with the average concentrations of these amino acids in juice of 'Malling Seedling' cv. (0.62 mmol·l^{-1}, 1.22 mmol·l^{-1}, 2.71 mmol·l^{-1} and 0.37 mmol·l^{-1}, respectively). The average content of glycine in juice of 'Canby' cv. (0.38 mmol·l^{-1}) was significantly higher in comparison with the content of this amino acid in juice of 'Beskid' cv. (0.21 mmol·l^{-1}).

Glutamic acid and γ-aminobutyric acid dominated in black currant juices (Fig. 3). The content of glutamic acid in black currant juices in particular years was from 0.52 mmol·l^{-1} too 2.89 mmol·l^{-1} and γ-aminobutyric acid – from 0.61 mmol·l^{-1} to 1.36 mmol·l^{-1}. Trace concentrations of proline, methionine (Table 4), isoleucine, leucine, tyrosine, lysine and arginine were found.

Table 2. Contents of serine in berry juices in 1998, 1999, 2000
Tabela 2. Zawartości seryny w sokach z owoców jagodowych badanych w latach 1998, 1999, 2000

Type of juice Rodzaje soków	Fruit variety Odmiany owoców	Serine, mmol·l^{-1} – Seryna, mmol·l^{-1}			
		year of fruit harvest lata zbioru owoców			average średnie
		1998	1999	2000	
Strawberry juice Sok z truskawek	Senga	0.48	0.28	0.16	0.31 ^{A} ± 0.16
	Ducat	0.47	0.25	0.27	0.33 ^{A} ± 0.12
	Marmolada	0.36	0.20	0.27	0.28 ^{A} ± 0.08
Raspberry juice Sok z malin	Beskid	0.84	0.58	0.98	0.80 ^{BC} ± 0.20
	Canby	1.43	0.81	1.14	1.13 ^{CD} ± 0.31
	Malling Seedling	1.20	1.07	1.40	1.22 ^{D} ± 1.17
Black currant juice Sok z czarnych porzeczek	Ben Lomond	0.32	0.12	0.18	0.21 ^{A} ± 0.10
	Titania	0.35	0.16	0.28	0.26 ^{A} ± 0.10
	Ojebyn	0.48	0.16	0.27	0.30 ^{A} ± 0.16
Red currant juice Sok z czerwonych porzeczek	Rondom	0.53	0.44	0.42	0.46 ^{AB} ± 0.06
	Jonker	0.20	0.19	0.26	0.22 ^{A} ± 0.04
	Holenderska	0.22	0.22	0.26	0.23 ^{A} ± 0.02

Values in the columns with different letters are significantly different at α = 0.05.
Wartości w kolumnach oznaczone różnymi literami różnią się istotnie przy α = 0,05.

The main amino acids in red currant juices were: glutamic acid, alanine, and γ-aminobutyric acid (Fig. 4). Concentrations of glutamic acid in red currant juices in particular years ranged from 0.63 mmol·l^{-1} to 7.67 mmol·l^{-1}, alanine – from 0.24 mmol·l^{-1} to 2.06 mmol·l^{-1} and γ-aminobutyric acid – from 0.47 mmol·l^{-1} to 1.47 mmol·l^{-1}. Trace concentrations of methionine (Table 4), isoleucine, leucine, tyrosine and lysine were found. From statistical point of view, the average glutamic acid and arginine contents for three years of examinations in juice of 'Rondom' cv. (5.07 mmol·l^{-1} and 0.48 mmol·l^{-1}, respectively) were significantly higher in comparison with the average contents of these amino acids in juice of 'Jonker' cv. (1.11 mmol·l^{-1} and 0.00 mmol·l^{-1}, respectively) and in juice of 'Holenderska' cv. (0.66 mmol·l^{-1} and 0.04 mmol·l^{-1}, respectively). Also the average concentration of alanine in juice of 'Rondom' cv. (1.46 mmol·l^{-1}) was significantly higher than the average concentration of this amino acid in juice of 'Holenderska' cv. (0.34 mmol·l^{-1}).

Concentrations of threonine, serine, proline, glycine, valine, methionine, isoleucine, leucine, tyrosine, γ-aminobutyric acid, histidine, lysine and arginine determined in present examinations in particular years in berry juices were similar to those found by Wallrauch and Faethe [1988]. Instead, in strawberry, raspberry and black currant juices significantly higher concentrations of aspartic acid were determined in comparison with those published by Wallrauch and Faethe [1988]. Berry juices contained significantly higher level of glutamic acid and red currant juices – lower level of alanine than values published by Wallrauch and Faethe [1988].

Table 3. Contents of valine in berry juices in 1998, 1999, 2000
Tabela 3. Zawartości waliny w sokach z owoców jagodowych badanych w latach 1998, 1999, 2000

Type of juice Rodzaje soków	Fruit variety Odmiany owoców	Valine, mmol·l^{-1} – Walina, mmol·l^{-1}			
		year of fruit harvest lata zbioru owoców			average średnie
		1998	1999	2000	
Strawberry juice Sok z truskawek	Senga	0.07	0.09	0.06	0.07 ^{A} ± 0.02
	Ducat	0.13	0.11	0.10	0.11 ^{AB} ± 0.02
	Marmolada	0.05	0.08	0.06	0.06 ^{A} ± 0.02
Raspberry juice Sok z malin	Beskid	0.20	0.17	0.23	0.20 ^{AB} ± 0.03
	Canby	0.42	0.18	0.22	0.27 ^{BC} ± 0.13
	Malling Seedling	0.37	0.26	0.48	0.37 ^{C} ± 0.11
Black currant juice Sok z czarnych porzeczek	Ben Lomond	0.07	0.08	0.12	0.09 ^{A} ± 0.03
	Titania	0.19	0.14	0.23	0.19 ^{AB} ± 0.05
	Ojebyn	0.26	0.12	0.20	0.19 ^{AB} ± 0.07
Red currant juice Sok z czerwonych porzeczek	Rondom	0.18	0.18	0.14	0.17 ^{AB} ± 0.02
	Jonker	0.05	0.10	0.15	0.10 ^{A} ± 0.05
	Holenderska	0.06	0.08	0.09	0.08 ^{A} ± 0.02

Values in the columns with different letters are significantly different at $\alpha = 0.05$.
Wartości w kolumnach oznaczone różnymi literami różnią się istotnie przy $\alpha = 0{,}05$.

According to Code of Practice [1996], authentic strawberry juice should contain 0.11-1.88 mmol·l^{-1} of aspartic acid, 0.14-1.7 mmol·l^{-1} of glutamic acid and maximum 0.27 mmol·l^{-1} of glycine, whereas in our examinations contents of aspartic acid, glutamic acid and glycine, in juices of different strawberry varieties were higher than estimated standards. The highest exceeding of standard values was found in case of aspartic acid – juice of 'Senga' cv. in 1999 contained by 253.2% higher level of aspartic acid than the highest permissible value.

In agreement with Code of Practice [1996], content of aspartic acid in non-adulterated black currant juice should be 0.15-0.75 mmol·l^{-1}, serine – 0.14-1.1 mmol·l^{-1}, glutamic acid – 0.27-1.5 mmol·l^{-1}, proline – 0.09-0.87 mmol·l^{-1}, alanine – 0.39-2.02 mmol·l^{-1}, valine – 0.09-0.51 mmol·l^{-1}, tyrosine – maximally 0.17 mmol·l^{-1}, γ-aminobutyric acid – 0.68-3.3 mmol·l^{-1} and arginine – 0.06-0.8 mmol·l^{-1}. In present examinations, in juices of different black currant varieties, higher concentrations of aspartic acid, glutamic acid and tyrosine and lower concentrations of serine, proline, alanine, valine, γ-aminobutyric acid and arginine were found in comparison with standard values published in Code of Practice [1996].

Table 4. Contents of methionine in berry juices in 1998, 1999, 2000
Tabela 4. Zawartości metioniny w sokach z owoców jagodowych badanych w latach 1998, 1999, 2000

Type of juice Rodzaje soków	Fruit variety Odmiany owoców	Methionine, mmol·l^{-1} – Metionina, mmol·l^{-1}			
		year of fruit harvest lata zbioru owoców			average średnie
		1998	1999	2000	
Strawberry juice Sok z truskawek	Senga	0.04	0.03	0.04	0.04 ^{A} ± 0.01
	Ducat	0.04	0.03	0.03	0.03 ^{A} ± 0.01
	Marmolada	0.00	0.03	0.03	0.02 ^{A} ± 0.02
Raspberry juice Sok z malin	Beskid	0.05	0.13	0.13	0.10 ^{B} ± 0.05
	Canby	0.06	0.07	0.08	0.07 ^{AB} ± 0.01
	Malling Seedling	0.06	0.09	0.15	0.10 ^{B} ± 0.05
Black currant juice Sok z czarnych porzeczek	Ben Lomond	0.07	0.06	0.08	0.07 ^{AB} ± 0.01
	Titania	0.05	0.06	0.12	0.08 ^{AB} ± 0.04
	Ojebyn	0.10	0.12	0.11	0.11 ^{B} ± 0.01
Red currant juice Sok z czerwonych porzeczek	Rondom	0.00	0.06	0.05	0.04 ^{A} ± 0.03
	Jonker	0.00	0.04	0.07	0.04 ^{A} ± 0.04
	Holenderska	0.00	0.04	0.04	0.03 ^{A} ± 0.02

Values in the columns with different letters are significantly different at $\alpha = 0.05$.
Wartości w kolumnach oznaczone różnymi literami różnią się istotnie przy $\alpha = 0{,}05$.

Code of Practice [1996] does not define permissible contents of particular amino acids in raspberry juice and red currant juice. Therefore, it is necessary to complete Code of Practice [1996] with standard contents of amino acids which are used for estimation of berry juice authenticity.

Differences between amino acid concentrations determined in the present paper and published in Code of Practice [1996] could result from differences in techniques of amino acid determinations, using liquid chromatography. The differences referred to methods of sample preparation and conditions of chromatographic separations. Achieved in present examinations higher contents of some amino acids might resulted from the fact that in juices besides free amino acids, also these, which arised from acid hydrolysis of samples, removed from protein to be sure, but not free of peptide were determined. Probably, asparagine and glutamine hydrolyzed to aspartic acid and glutamic acid, therefore higher concentrations of aspartic acid and glutamic acid were observed. However, if contents of aspartic acid and asparagine, as well as glutamic acid and glutamine published in Code of Practice [1996] are summed up, it appears that these values agree with contents of aspartic acid and glutamic acid found in the present paper.

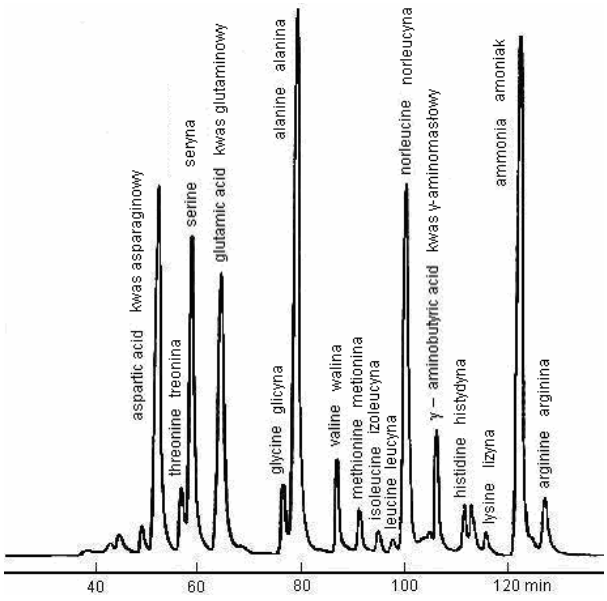

Fig. 2. Chromatogram of amino acids contained in raspberry juice of 'Beskid' cv. harvested in 2000
Rys. 2. Chromatogram aminokwasów zawartych w soku malinowym odmiany 'Beskid' ze zbioru w 2000 roku

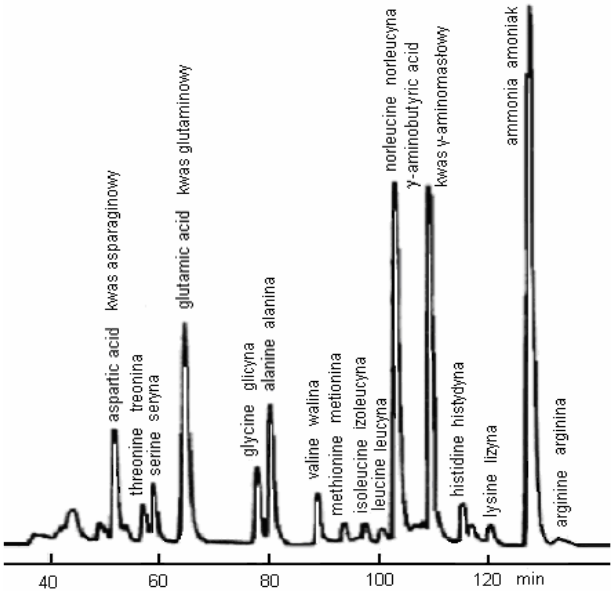

Fig. 3. Chromatogram of amino acids contained in black currant juice of 'Ben Lomond' cv. harvested in 2000
Rys. 3. Chromatogram aminokwasów zawartych w soku z czarnych porzeczek odmiany 'Ben Lomond' ze zbioru w 2000 roku

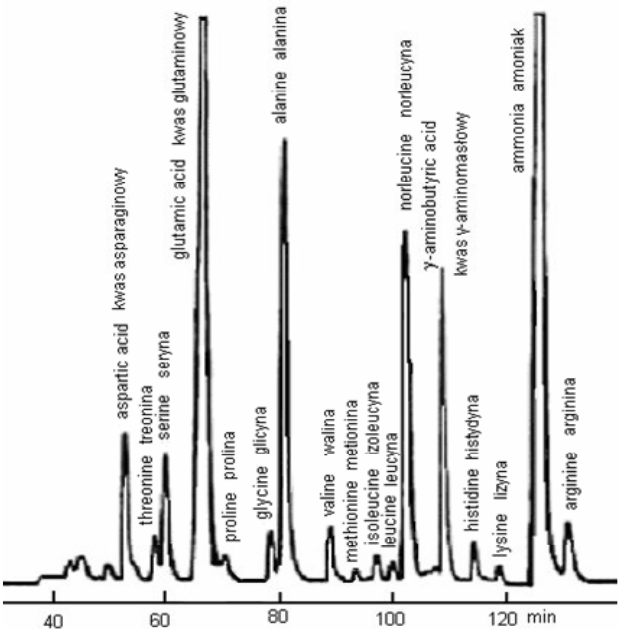

Fig. 4. Chromatogram of amino acids contained in red currant juice of 'Rondom' cv. harvested in 2000
Rys. 4. Chromatogram aminokwasów zawartych w soku z czerwonych porzeczek odmiany 'Rondom' ze zbioru w 2000 roku

Some amino acids occurred in different concentration ranges in berry juices. Contents of serine (Table 2), valine (Table 3) and methionine (Table 4) in raspberry juices in particular years were from 0.58 mmol·l^{-1} to 1.43 mmol·l^{-1}, from 0.17 mmol·l^{-1} to 0.48 mmol·l^{-1} and from 0.05 mmol·l^{-1} to 0.15 mmol·l^{-1}, respectively, and in strawberry juices – from 0.16 mmol·l^{-1} to 0.48 mmol·l^{-1}, from 0.05 mmol·l^{-1} to 0.13 mmol·l^{-1} and from 0.00 mmol·l^{-1} to 0.04 mmol·l^{-1}, respectively. Therefore, decrease of serine, valine and methionine concentrations could point out to adulteration of raspberry juice with strawberry juice. Raspberry juices contained from 1.34 mmol·l^{-1} to 15.61 mmol·l^{-1} of aspartic acid (Table 1) and from 0.58 mmol·l^{-1} to 1.43 mmol·l^{-1} of serine (Table 2), instead of red currant juices – from 0.23 mmol·l^{-1} to 0.92 mmol·l^{-1} of aspartic acid and from 0.19 mmol·l^{-1} to 0.53 mmol·l^{-1} of serine. Thus the decrease of aspartic acid and serine contents in raspberry juice declared as authentic could indicate the addition of red currant juice or another origin contained lower concentrations of these amino acids. Contents of aspartic acid (Table 1) and methionine (Table 4) in black currant juices were from 0.18 mmol·l^{-1} to 1.54 mmol·l^{-1} and from 0.05 mmol·l^{-1} to 0.12 mmol·l^{-1}, respectively, and in strawberry juices – from 1.68 mmol·l^{-1} to 6.64 mmol·l^{-1} and from 0.00 mmol·l^{-1} to 0.04 mmol·l^{-1}, respectively. Therefore, increase of aspartic acid concentration and decrease of methionine concentration could be the indicator of addition of strawberry juice to black currant juice. On the other hand, adulteration of black currant juice with red currant juice cannot be detected on the base of amino acid contents, because particular amino acids occurred in these juices at similar concentrations.

CONCLUSIONS

1. Significantly higher aspartic acid and glutamic acid concentrations of standard values published in Code of Practice [1996] were found in examined strawberry and black currant juices.

2. It is necessary to complete Code of Practice [1996] of permissible contents of particular amino acids in raspberry juice and red currant juice.

3. Selected amino acids can be used for estimation of berry juices authenticity. Serine, valine and methionine can be the indicator of addition of strawberry juice to raspberry juice, aspartic acid and serine – addition of red currant juice to raspberry juice and aspartic acid and methionine – addition of strawberry juice to black currant juice.

4. Adulteration of black currant juice with red currant juice cannot be detected on the base of amino acid contents.

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ZASTOSOWANIE ANALIZY AMINOKWASÓW DO OCENY AUTENTYCZNOŚCI SOKÓW Z OWOCÓW JAGODOWYCH

Streszczenie. W niniejszej pracy oznaczono zawartości wolnych aminokwasów: kwasu asparaginowego, treoniny, seryny, kwasu glutaminowego, proliny, glicyny, alaniny, waliny, metioniny, izoleucyny, leucyny, tyrozyny, kwasu γ-aminomasłowego, histydyny, lizyny i argininy w sokach otrzymanych z trzech odmian truskawek ('Senga', 'Ducat', 'Marmolada'), malin ('Beskid', 'Canby', 'Malling Seedling'), czarnych porzeczek ('Ben Lomond', 'Titania', 'Ojebyn') i czerwonych porzeczek ('Rondom', 'Jonker', 'Holenderska'). Badania wykonano w trzech kolejnych latach: 1998, 1999 i 2000, stosując metodę HPLC. Porównano otrzymane zawartości aminokwasów z wartościami standardowymi zawartymi w Kodeksie Praktyki. W badanych sokach truskawkowych i z czarnych porzeczek stwierdzono znacznie wyższe stężenia kwasu asparaginowego i kwasu glutaminowego od wartości standardowych podanych w Kodeksie Praktyki. Wybrane aminokwasy mogą być wykorzystane do oceny autentyczności soków z owoców jagodowych. Wskaźnikiem dodatku soku truskawkowego do soku malinowego może być seryna, walina i metionina, dodatku soku z czerwonych porzeczek do soku malinowego – kwas asparaginowy i seryna, a dodatku soku truskawkowego do soku z czarnych porzeczek – kwas asparaginowy i metionina. Na podstawie zawartości aminokwasów nie można wykryć zafałszowania soku z czarnych porzeczek sokiem z czerwonych porzeczek.

Słowa kluczowe: aminokwasy, HPLC, owoce jagodowe, soki, zafałszowania

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